

Process-directed self-assembly of copolymer materials

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The free-energy landscape of copolymer materials exhibits a multitude of metastable minima that correspond, e.g., to alternate periodic phases like hexagonally perforated lamellae, grain boundaries between domains of different orientations, or local defects. The barriers between these metastable states exceeds the thermal energy scale by far, resulting in protracted relaxation times. The thermodynamic stable morphology that corresponds to the absolute minimum often cannot be reached in experiments and simulations.

Process-directed self-assembly refers to strategies that reproducibly direct the kinetics of self-assembly into a desired (meta)stable morphology by temporal control of thermodynamic variables [1], e.g., temperature or pressure. This strategy allows to access new morphologies, e.g., the bicontinuous I-WP network morphology [1], that do not correspond to stable bulk phases or control the orientation of the microphase-separated domains [3]. In order to exploit this strategy an understanding of the non-equilibrium self-assembly process and its underlying free-energy landscape is required.

Using computer simulation of soft, coarse-grained models we illustrate different processing protocols, e.g., pressure jumps [1], solvent or temperature annealing protocols [2], roll-casting [3], or spray coating [4], and demonstrate how the non-equilibrium, unstable initial condition dictates the spinodal kinetics of structure formation into a desired morphology. Since the initial kinetics occurs on the same time scale as the relaxation of the molecular conformations, chain conformations cannot be assumed to be in equilibrium with the instantaneous densities -- an assumption that is invoked in dynamic self-consistent field calculations -- but additional, unconventional order-parameters, e.g., the variance of the lowest Rouse-modes [3] or the fraction of bridges in multiblock copolymers, are required to characterize the rapid structure evolution out of a non-equilibrium state into the nearest metastable morphology. In addition to the free-energy landscape as a functional of the densities and the additional order parameters also the single-chain kinetics plays an important role for selecting the nearest metastable morphology [1,3].

[1] Directing the self-assembly of block copolymers into a metastable complex network phase via a deep and rapid quench, M. Müller and D.W. Sun, Phys. Rev. Lett. 111, 267801 (2013)

[2] Defect removal in the course of directed self-assembly is facilitated in the vicinity of the order-disorder transition, W.H. Li, P.F. Nealey, J.J. de Pablo, and M. Müller, Phys. Rev. Lett. 113, 168301 (2014)

[3] Alignment of copolymer morphology by planar step elongation during spinodal self-assembly, M. Müller and J. Tang, Phys. Rev. Lett. 115, 228301 (2015)

[4] Process-directed self-assembly of multiblock copolymers: solvent casting vs spray coating, Q. Tang, J. Tang, and M. Müller, Eur. Phys. J. Special Topics in press 10.1140/epjst/e2016-60121-6